



Controlled burn and immediate mobilization of potentially toxic elements in soil, from a legacy mine site in Central Victoria, Australia

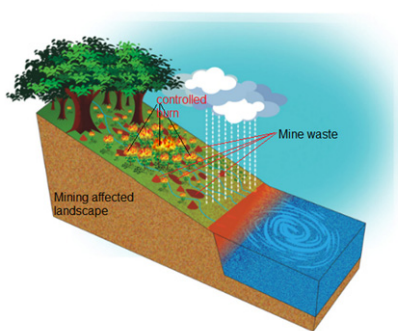
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HIGHLIGHTS

- Legacy gold mining sites have elevated potentially toxic element (PTE) concentrations.
- PTEs are sequestered in the soil organic matter and vegetation, limiting its mobility.
- Controlled burns remobilized PTEs such as Zn, Mn, Cd & Hg.
- Liberated PTE mobilized to soil, and may be to air & water environment.
- Controlled burns should be carefully considered as a forest management strategy.

GRAPHICAL ABSTRACT



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ABSTRACT

Conducting controlled burns in fire prone areas is an efficient and economic method for forest management, and provides relief from the incidence of high severity wild fires and the consequent damage to human property and ecosystems. However, similar to wild fires, controlled burns also affect many of the physical and biogeochemical properties of the forest soil and may facilitate remobilization of potentially toxic elements (PTEs) sequestered in vegetation and soil organic matter. The objective of the current study is to investigate the mobilization of PTEs, in Central Victorian forest soils in Australia after a controlled burn. Surface soil samples were collected two days before and after the controlled burn to determine the concentration of PTEs and to examine the physicochemical properties. Results show that As, Cd, Mn, Ni and Zn concentrations increased 1.1, 1.6, 1.7, 1.1 and 1.9 times respectively in the post-burn environment, whereas the concentrations of Hg, Cr and Pb decreased to 0.7, 0.9 and 0.9 times respectively, highlighting considerable PTE mobility during and after a controlled burn. Whilst these results do not identify very strong correlations between physicochemical properties of soil and PTEs in the pre- and post-burn environments, PTEs themselves demonstrated very strong and significant correlations. The mobilization of As, Hg and other toxic elements raise potential health concerns as the number of controlled burns are projected to increase in response to climate change. Due to this increased level of PTE release and remobilization, the use of any kinds of controlled burn must be carefully considered before being used as a forest management strategy in mining-affected landscapes which include areas with high PTE concentrations.

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1. Introduction

Potentially toxic elements (PTEs) such as As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn, contribute to contamination in soil and aquatic

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environments, and this is of great concern due to the immediate risks to human and ecosystems health and the perceived persistency of these elements in the environment (Tijani et al., 2005; Zhuang et al., 2014; Soliman et al., 2015). Gold and other metal mining activities may contribute to significant PTE contamination in many rural areas (Sultan, 2006, 2007; Taylor et al., 2010; Pearce et al., 2012; Krishna et al., 2013). Mining, milling and grinding operations, which result in concentrations of fine ore materials, together with the subsequent disposal of tailings and mine and mill waste water, are a source of water, soil and air contamination in the vicinity of the mine site (Schneider et al., 2007; Navarro et al., 2008; Esshaimi et al., 2012; Doronila et al., 2014). This is particularly significant in legacy mine sites, where environmental regulations were neither enforced during active mining, nor at the time of mine closure. For example, Central Victoria, in Australia has a long history of gold mining since 1850 (McDonald and Powell, 2008) and has significantly contributed to the economy with the region producing more than 2500 t of gold (EER, 2015). However, mine closure left tonnes of mine waste materials rich in PTEs in the surface soils with resultant contamination of soils, water, air, and plants (Sultan, 2006, 2007; Pearce et al., 2010, 2012; Martin et al., 2014, 2016). Recent studies have reported As absorption by adults, specifically children living close to these abandoned sites in Central Victorian soils, are of growing concern (Pearce et al., 2010, 2012; Martin et al., 2013, 2014). Furthermore, most of these mine waste materials are located in forest areas, and are un-rehabilitated, leaving them prone to mechanical dispersion, which may increase their mobility and bioavailability.

Forest ecosystems generally absorb PTEs from natural and anthropogenic activities as most have an affinity for soil organic matter (SOM). This is particularly the case for Hg, Cu and Pb (Wei and Yang, 2010; Shcherbov, 2012; UNEP, 2013), and the rate of absorption depends on the amount of SOM, the fixation to clay minerals, local adsorption and desorption processes and their correlation with Al and Fe hydroxides and Mn oxides (Sipos et al., 2005; Kabata-Pendias, 2004, 2010; Reis et al., 2015). After entering forest ecosystems, PTEs may concentrate in the organic layers of the soil, sequester in sediments, form compounds with SOM and may be absorbed by plants and hence become immobile in the system (Grigal, 2003; Hernandez et al., 2003; Biswas et al., 2007; Obrist et al., 2008; Friedli et al., 2009; Shcherbov, 2012). Grigal (2003) reported that 90% of the Hg in the forest ecosystem is found to be associated with SOM in the forest floor, and in addition to Hg, other PTEs such as Cr, Cu and Pb are also found to be strongly bound in the system, whereas, Cd, Co, Mn, Ni and Zn are weakly bound (Tipping, 1998; Lawlor and Tipping, 2003). When forest fire, either as a wild or controlled burn occurs, combustion of the vegetation and SOM causes soil property alterations, which can release the sequestered elements from the system and become labile and will be able to remobilize, mostly through ash and smoke (Odigie and Flegal, 2011, 2014). This is particularly significant in the Central Victoria region of Australia, as the region is prone to wild fires due to weather patterns and types of dense vegetation and controlled burns are regularly applied in the region as a standard fire-risk reduction strategy.

Controlled or prescribed burning is the deliberate application of fire to forest fuels or agricultural lands, mainly in autumn or spring (but may also be applied in late winter) under stipulated settings to ensure such that well-defined targets are achieved (Wade et al., 1989). Preparation for agriculture and tree restoration, control of weeds and insects populations, wildlife habitat management, maintenance of biodiversity, fuel level reduction and other land management practices are usually the intention of careful application of controlled burns (Fernandez and Botelho, 2003). In general, controlled burns are of low to moderate intensity, and consume most of the forest floor layers and understory vegetation, with no or little damage to the canopy trees (Úbeda et al., 2005). The burn reduces the occurrence of a subsequent wildfire, or can reduce its intensity, by reducing the fuel loads both vertically and horizontally, which directly improve the fire control measures (Hatten et al., 2005). Therefore, controlled burning is considered to be a valuable tool in

forest protection and wildfire mitigation (Fernandez and Botelho, 2003; Certini, 2005; Castellinou et al., 2010) and is practised in the fire prone forest landscapes in many countries in Europe, North and South America and Australia.

Fire intensity equates to the release of thermal energy as a result of the physical combustion process, and is defined as the measure of time averaged energy flux (Keeley, 2009). Severity is the response of an ecosystem to fire, which is gauged by the product of fire intensity and residence time (Certini, 2005; Neary et al., 2005; Keeley, 2009). Physically fire intensity is quantified using temperature, flame height, duration of fire, and the emission of pyrogenic gases (Lentile et al., 2006). It is mostly controlled by fuel (vegetation) types and density, moisture content in the fuel, weather pattern, topography and other local factors (DeBano et al., 1998). Intensity can be measured by measuring the fire temperature using thermocouples or can be inferred from the observation of flame length and fire spread rate (Smith and Wooster, 2005; Dennison, 2006). Fire severity provides information about how fire intensity affects ecosystems and is sometimes used wrongly as a synonym for fire intensity (Certini, 2005; Keeley, 2009). Fire severity measures are based on number of methodologies, and among them, observation of ash colour is significant (Úbeda et al., 2009; Pereira et al., 2011). Another relevant term is 'burn severity', which sometimes is mistakenly used for fire severity. Burn severity identifies the impact of fire on soil and plants when the fire is extinguished, and is related to the post-fire phase. Further fire-related information is available in a number of studies (Certini, 2005; Neary et al., 2005; Lentile et al., 2006; De Santis and Chuvieco, 2007; Murphy et al., 2008; Safford et al., 2008; Keeley, 2009; Parsons et al., 2010; Mataix-Solera et al., 2011).

The intrinsic character of any kind of forest fire is the complex process of heat release during biomass combustion (Bento-Gonçalves et al., 2012). The burning biomass and ash can transfer heat to the soil surface, and it may reach up to 30 cm depth in the case of high severity wild fires (DeBano, 2000). As a result, fire can change the physicochemical, mineralogical and biological properties of the forest soil and surface materials (Certini, 2005; Verma and Jayakumar, 2012). However, most of these alterations are ephemeral, such as pH and electrical conductivity (EC) (Arocena and Opio, 2003), with only a few being perpetual (Certini, 2005), and all alternations depend on fire severity (Dzwonko et al., 2015). Similar to wildfires, controlled burns also affect soil properties, but, often to a limited extent (Arocena and Opio, 2003; Castro et al., 2011; Pereira et al., 2011; Melendez-Perez et al., 2014). Fire typically increases pH values and EC of the soil, makes significant alterations in SOM levels, decreases soil permeability and porosity, resulting in the reduction of hydraulic conductivity and causing considerable loss in nutrient levels (Certini, 2005; Verma and Jayakumar, 2012). With these soil property alterations, many authors reported that wild fire is able to release PTEs (metals) from plants and soil organic matter from their sequestered phase (Odigie and Flegal, 2011, 2014; Burton et al., 2016; Kristensen et al., 2014; Odigie et al., 2016). For example, Ignatavicius et al. (2006) reported an increase in concentrations of Pb, Cu, and Zn (21 to 74%) in Lithuanian river waters (August–September 2002) one month after a series of 497 forest and peat bog fires in the region. Similarly, remobilization of Fe, Mn and Hg after the 2009 Station Fire in Los Angeles, USA was observed (Burton et al., 2016). In conjunction with this, Kristensen et al. (2014) reported the remobilization of natural and industrial Pb (4 to 23 mg kg⁻¹) after three wild-fires in Australia (the Tostaree Fire in Victoria, at Red Hill and the Kelmscott Fire in Western Australia). In addition to this, Odigie et al. (2016) linked the occurrence of PTEs in the sediments of the Lake Thomson in Chile with forest fires which occurred in mid 1900s. Though these studies were directed to establish the consequence of wild fire on PTE mobility, there is a general lack of research in the global literature on the effects of controlled burns in PTE mobility, specifically on legacy mining landscapes.

Forest fire and subsequent PTE mobilization is particularly pertinent to legacy mining areas because of the presence of an extensive volume of tailings and other mine waste materials with elevated PTE

concentrations. Many such mining affected landscapes are located in forest regions, as in Central Victoria, which are prone to frequent and uncontrolled wild fires and their incidence and severity are predicted to increase because of climate change effects, which may require more controlled burns (Hennessy et al., 2005; Westerling et al., 2006). Given that fires are able to mobilize PTEs from SOM and vegetation, the objective of the current study is to (i) determine the mobility of 10 PTEs (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn) which are toxic to human health and ecosystems, in the surface soils of a legacy mine site (Maldon) in the Central Victorian region of Australia, after a controlled burn, and (ii) to assess the change in soil physicochemical characteristics immediately after fire. Assessing the mobility of PTEs in any legacy mine site after a controlled burn is necessary as the excess PTE concentrations can influence animals, and plants as well as human health (Hindwood et al., 2003; Kelly et al., 2006; Nunes et al., 2017). This is particularly significant in the study area as it is adjacent to a residential area and the Central Victorian forest catchment provides potable water resources to a number of local communities. The outcome of this study will be useful for environmental scientists and land managers in reviewing the potential for contamination after a controlled burn, and the result will provide guidance to post-fire watershed management practices in terms of water quality, which will be useful for water distribution managers. Results will also be useful for local, state and national authorities and environmental agencies to assist better environment and fire management practices within legacy mining landscapes. In addition, this work may also assist un-rehabilitated mine site management in other fire prone states or countries. Although it is recognised that the study area is relatively small, the mobilization of PTEs during or after any kind of forest fire (including controlled burns) is significant because more than a million un-rehabilitated legacy mine sites exist across the globe, and many of them are in fire prone forest areas (UNEP, 2001).

2. Materials and methods

2.1. Description of the study area

Maldon, a legacy gold mining area, is located 145 km NW of the city of Melbourne and 40 km SW of the City of Greater Bendigo, where small

scale mining was started in 1853 and subsequently, production moved to larger mining companies. Mining was stopped in 1926 due to difficulties encountered in the mining process. In this historical mining period, the Maldon area produced more than 56 t of gold from a number of mining sites (Cherry and Wilkinson, 1994), and was the eighth largest City in the State of Victoria in Australia (Egold, 2017). Early gold extraction techniques used cradle and gold pan to separate the gold from alluvium, but later moved to puddling, quartz reef mining, deep lead mining and various forms of sluicing (Egold, 2017). Among these approaches, quartz reef mining was the most widely practiced, requiring construction and operation of crushing mills and stamping batteries. Today, constructed adits, shafts and open cut mining trenches used to access the sulphide bearing ore, can be seen in Maldon as mining remnants (Cherry and Wilkinson, 1994; Maldon, 2017). The mining resulted in the accumulation of tonnes of mine waste materials of many kinds on the surface, often seen as mullock heaps. A specific mine site located east of the Union Hill mine and west and south of the Stump Street was selected for the controlled burn influenced PTE mobility study (Fig. 1). It comprises 20 acres of land which falls under the jurisdiction of public land (State forest) and is adjacent to number of residences.

The study area experiences cold wet winters (7.5–20.5 °C) and warm dry summers (16.4–40.3 °C) (Taylor and Alley, 2001; BoM, 2017), with an annual average rainfall of 540 mm (BoM, 2017). The major vegetation in the area is a mix of native and introduced species including *Ulex europaeus* (Gorse), *Cassinia arcuta* (Chinese shrub), *Juncus acutus* (Shirp), *Asphodelus fistulosus* (Onida), *Acacia pycnantha*, and *Eucalyptus radiata*.

A creek line runs in an easterly direction, passing along the middle of the study area. The northern half of the study area slopes slightly towards the south, and the southern half slopes (slightly) towards north, thus directing all the runoff to the creek. In this public land, disturbed overburden with burrows, soil heaps, and scattered quartz fragments demonstrate legacy gold mining activities. The occurrence of moderate-to-highly disturbed (by legacy mining) soils, together with more than a century's accretion of old mining waste materials in the area, makes it ideal for evaluating legacy mining impacts on the environment. The study area is notable as it is adjacent to residential areas (Fig. 1) and has a creek running through middle of this public land

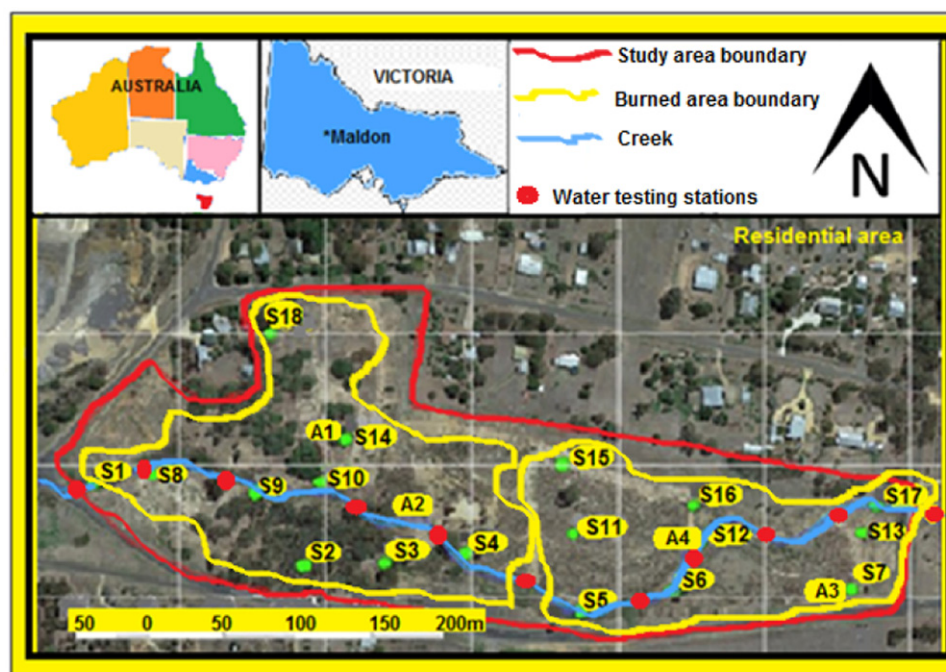


Fig. 1. Location of the study area with soil sampling (S1 to S18), ash sampling (A1 to A4) and water testing (red spot along the creek) stations. Proximity to housing is noted. >80% of the study area has been affected by controlled burns.

that could carry contaminants 1.6 km to downstream residential areas and 8 km to a small water body and 30 km to a large reservoir (McKay reservoir).

2.2. Controlled burn, soil sampling and analysis

Forest floor material, also called detritus, is a substantial segment of the forest ecosystem, and is mainly composed of organic matter, mixture of minerals, biogenic substance and water soluble organic compounds, which act as a potential reservoir of toxic elements (Shcherbov, 2012). In the Maldon study area, significant growth of an invasive species Gorse (*Ulex europaeus*) is the major vegetation, and controlled burning is a standard fire risk reduction and weed management strategy. The investigated burn was carried out by the State Department of Environment Land Water and Planning (DELWP) and Parks Victoria fire crews on 20th August 2015 (Fig. 2), which was the end of the winter season. The day was calm and sunny with wind moving in a SW direction. The fire was started around 10:00 am by the Parks Victoria fire crews, at the western part of the study area and moved to east. Immediately after ignition, the fire grew rapidly due to the presence of a significant fuel load (Fig. 2) and the smoke moved in a SW direction. Approximately one and a half hour was more than enough to burn the majority of the forest floor fuel load. While the seemingly intense fire lasted for only several minutes in one location and subsided normally, slow burning of plant materials was observed up to three days after ignition. The fire burned most of the shrub type vegetation (<2 m in height), including Chinese shrub (*Cassinia arcuata*), Onida (*Asphodelus fistulosus*), and also the ground cover litter (Fig. 3). More than 80% of the study area was affected by the fire, as it was completely covered by vegetation and litter as a result of there being no history of any kind of fire in the area (information from DELP). There were high quantities of ash observed in some pockets in the burned area, where thick vegetation, particularly tree branches, were burnt. In some spots, it was grey in colour, indicating the moderate to high fire severity (Úbeda et al., 2009). The fire left all canopies of the eucalyptus radiata untouched, but consumed some of the barks and roots, and all of the shrubs were completely burned (Fig. 3).

Surface soil and ash samples are important in this study as they bear relevant products of the fire event, and can be mobilized by precipitation and subsequent surface runoff, wind-borne transport, and can cause negative impacts on human and other animals (Schneider et al., 2007). Furthermore, the majority of the PTEs in the forest ecosystem are concentrated in the organic layers of the soil in the forest floor, since they have an affinity for soil organic matter (SOM) (Hernandez et al., 2003; Shcherbov, 2012). To examine the PTEs mobility in the surface soils after the controlled burn, 18 surface soil samples (not >3 cm deep) were collected two days before the burn and 18 samples were

collected two days after the burn from the same sampling stations (S1 to S18: Fig. 1), using the STAR sampling method with trace metal clean technique procedures (Ritson et al., 1999; Soto-Jimenez et al., 2006; Taylor et al., 2010; Odigie and Flegal, 2011). In addition to the soil samples, four ash samples (A1 to A4, Fig. 1) were also collected, having a maximum of approximately 200 g from each site.

In most of the sampling stations, post-burn soil samples represent a mix of both soil and ash particles. After removing the debris and rock particles, approximately 1 kg of bulk surface soil samples were collected within an area of 1600 cm² (40 cm × 40 cm) from each station, two days before the burn and two days after the burn. The pre-burn and post-burn sampling stations were selected as close as possible (not 5–10 cm). Soon after collection, at each sampling station (S1 to S18) the soil samples (also ash) were carefully transferred to clean, dry and labelled polyethylene containers and carried to the Federation University Australia soil and water laboratory. Samples were placed in an oven (Memmert GMBH-D 8540) at 60 °C for 24 h. After removing the rock pieces, oven dried samples were hand crushed and sieved through a 2 mm stainless steel sieve. The pre-burn and post-burn sieved samples (<2 mm) were stored in air-tight polyethylene containers until all analyses were completed. Soil pH and EC were determined with standard analytical procedures (US-EPA 9045D & 9050A respectively) using a pH meter (WP-80) and an EC meter (Hanna HI-8633) (Rayment and Lyons, 2014). SOM and carbonate content (both as percentages) were determined with Loss on Ignition (LOI) method using a muffle furnace (Eurothem 2132) (Rayment and Lyons, 2014). The pH and EC of creek water sample were measured at 11 stations along the creek (W1 to W11 Fig. 1) with an Horiba multi-parameter water quality meter (IC-U51-2M), two days before the burn and two days after the burn. Ash samples were also collected from four different stations (A1 to A4) (Fig. 1) and analysed for PTE concentrations and physicochemical properties. 10 g of soil and ash samples were used for pH and EC analysis and <2 g were used for soil organic matter and carbonate content analysis.

PTE concentrations in soil and ash were determined by Ultra-Trace Level Methods, using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) with Aqua Regia Digestion (GEO-AR01) in a NATA (National Association of Testing Authorities) accredited laboratory (Accreditation No. 825). Dried and sieved soil samples were milled using stainless steel bowls and a milled sample of 0.5 g was used for PTE analysis. The soil samples were digested with aqua regia in a graphite heating block and allowed to cool. The resulting solution was diluted with deionized water, thoroughly mixed and analysed by ICP-AES. Immediately after this analysis, the results were revised for elevated concentration of Hg and diluted appropriately. These diluted and mixed samples were then analysed by ICP-MS for the remaining potentially toxic elements and the results were corrected for inter-element spectral interference (Santoro et al., 2017). A similar analysis scheme was also conducted for ash samples with a similar amount (0.5 g) of samples.

2.3. Data analysis

The data were statistically analysed using SPSS (version 23) and R (version 3.4.1) software(s). Some descriptive statistics (minimum, maximum, range, median, percentiles (10th, 25th, 50th, 75th and 90th) and interquartile range (IQR)) of the soil properties such as pH, EC, SOM, carbonate content and PTE analysis were applied to the pre-fire and post-fire results.

Pre-burn soil sample data from the study area such as physicochemical properties including pH, EC, SOM, carbonate content and PTE concentrations were compared with corresponding post-burn sample data in order to establish the influence of controlled burn on the concentrations of PTEs in the soil and the physicochemical properties of the soil. Moreover, the pH and EC of creek water flowing through the middle of the study area were also compared. The Wilcoxon matched pair test was conducted to the pre-burn and the corresponding post-burn



Fig. 2. Controlled burn conducting in the Maldon study area (Victoria, Australia) on 20th August 2015.



Fig. 3. Showing a part of the study area before (left), during (middle) and after (right) the controlled burn.

data to verify if statistically significant differences existed between them, including water pH and EC. Spearman rank correlation coefficients were determined to obtain the relationships between the pre- and post-burn physicochemical properties of the soil and the corresponding concentrations of PTE in the soil/ash environment include relationship between the PTE themselves.

3. Results and discussion

3.1. Physicochemical characteristics of soil

The descriptive statistics included minimum, maximum, range, median, percentiles and interquartile range (IQR) of physicochemical properties of soil and water in two sampling periods (BF and AF) were depicted in Table 1. The post-burn soil samples demonstrated significantly higher pH ($p < 0.05$), EC ($p < 0.01$), and SOM ($p = 0.07$) compared with pre-burn soil samples with difference in values amounting to a factor of 1.2, 2.2, and 1.4 respectively. However, the carbonate content showed only minor variations in the pre- and post-burn

environment. In the case of creek water, at individual locations, pH may showed up to 3 units post-burn difference, however the median pH for all sampling stations calculated before and after the controlled burn show no statistically significant difference. Conversely, the median EC value of water samples showed significant ($p < 0.0001$) increase after the burn, with a difference up to $100 \mu\text{S cm}^{-1}$ being was observed.

3.1.1. Soil pH

The soil pH and its relationship with PTEs in soils have been noted by many authors, and it is generally agreed that pH is generally related to PTE mobility (Bergkvist et al., 1989; Violante et al., 2010), speciation (Drever, 1988), solubility and uptake by plants (Adriano, 1986; Breulmann et al., 2002). The solubility and mobility of PTEs increased with lowering the soil pH, but this change has been shown to decrease the organophilic characteristics of some PTEs (Drever, 1988).

The pre-burn and post-burn pH distribution is depicted in Fig. 4(a). In the post-burn soil environment, the soil acidity is slightly reduced compared to the pre-burn environment and the pH becomes slightly basic. Among the 18 sample stations, 12 stations (67%) showed increase

Table 1
Descriptive statistics (minimum, maximum, range, median, percentiles and interquartile range (IQR)) of pH, EC ($\mu\text{S cm}^{-1}$), SOM (%) and carbonate content (Carb%) of soils and pH and EC ($\mu\text{S cm}^{-1}$) of water samples, both from the pre-burn (before fire – BF) and post-burn (after fire – AF) environment ($N = 18$).

Soil								
	pH-BF	pH-AF	EC-BF ($\mu\text{S cm}^{-1}$)	EC-AF ($\mu\text{S cm}^{-1}$)	SOM-BF (%)	SOM-AF (%)	Carb-BF (%)	Carb-AF (%)
Minimum	3.6	3.8	95	174	4	3	0.8	0.6
Maximum	5.6	8.6	970	2800	42	33	2.4	2.4
Range	2.0	4.8	875	2626	38	31	1.7	1.9
Median	4.3	4.8	376	863	9	15	1.5	1.4
Percentiles								
10th	3.8	4.0	200	253	5	4	0.8	0.6
25th	3.9	4.3	238	423	7	9	1.1	1
50th	4.3	4.8	376	863	9	15	1.5	1.4
75th	5.1	6.4	553	1249	14	26	1.9	1.7
90th	5.3	8.1	939	2170	24	29	2.4	2.1
IQR	1.2	2.1	316	826	7	17.5	0.8	0.7
Creek water								
	pH-BF	pH-AF	EC-BF ($\mu\text{S cm}^{-1}$)	EC-AF ($\mu\text{S cm}^{-1}$)				
Minimum		6.8		6.1	63		67	
Maximum		9.1		11.0	172		275	
Range		2.6		4.9	109		208	
Median		7.7		7.8	123		170	
Percentiles								
10th		6.9		6.3	69		75	
25th		7.2		7.2	98		124	
50th		7.7		7.8	123		170	
75th		8.4		8.4	157		225	
90th		9.0		10.5	171		266	
IQR		1.2		1.2	59		101	

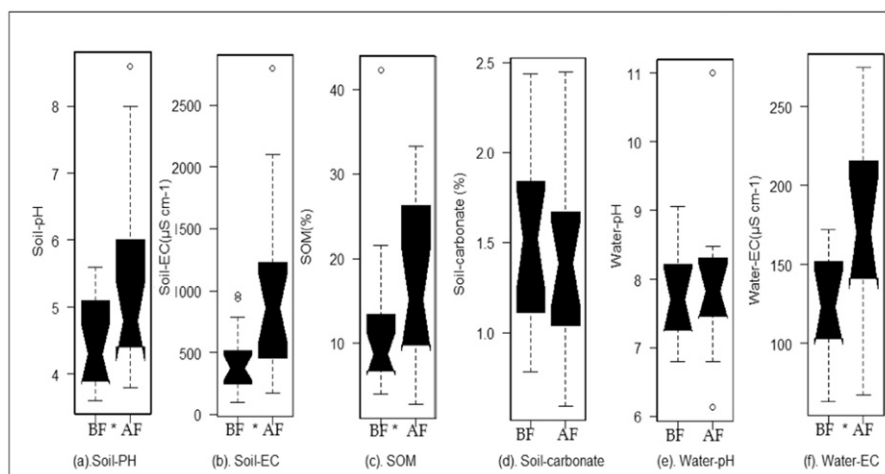


Fig. 4. Notched box plot showing (a) soil-pH, (b) soil-electrical conductivity (EC), (c) soil organic matter (SOM), (d) soil carbonate content, (e) water-pH and (f) water-EC observed before (BF) and after (AF) the controlled burn (NB: o represents outliers).

in pH value and 5 stations (28%) showed reduction in pH and one station (5%) showed no change in pH after the controlled burn. The highest pH variation observed is 3.7, followed by 3.5 and the lowest is 0.3 and no variation observed at sampling station S3. In two stations, post-burn pH increased to 7.6 and in one station pH increased to 8.6.

This increase in pH is observed at sampling stations where high amounts of ash were deposited during the burn due to the local increase in fuel load. It is thought that the increase in pH is mainly due to the release of large amounts of oxides, hydroxides, carbonates and cations through ash and the reduction in the production of organic acids as have been mentioned in other studies (Ulery et al., 1993; Khanna et al., 1994; Ulery et al., 1995; Certini, 2005; Goforth et al., 2005; Verma and Jayakumar, 2012). In similar works in other laboratories (Sever et al., 2001; Badía and Martí, 2003; Marcos et al., 2007) and field studies (Arocena and Opio, 2003; Úbeda et al., 2005; Campos et al., 2016) including controlled burn studies (Deluca and Zouhar, 2000; Arocena and Opio, 2003; Úbeda et al., 2005), there were also reported increase in soil pH after fire. This post-burn increase in soil pH is reported as ephemeral, as it has the tendency to step back to the pre-burn levels, after several months, although this has taken several years in some environment (Ulery et al., 1993, 1995; Kim et al., 2003; Certini, 2005; Jovanovic et al., 2011).

3.1.2. Electrical conductivity (EC)

In the case of EC (Fig. 4(b)), thirteen sample stations (72%) showed increase in EC values, and five stations (28%) showed decrease after the burn. The highest EC variation observed is $2011 \mu\text{S cm}^{-1}$, followed by $2005 \mu\text{S cm}^{-1}$ and $1026 \mu\text{S cm}^{-1}$ and the lowest is $28 \mu\text{S cm}^{-1}$. In a similar mechanism to pH change, the increase in post-fire soil EC is linked to the combustion of vegetation, SOM and the associated deposition of ash, which release of high amounts of oxides, hydroxides, cations and carbonates (Ulery et al., 1993; Khanna et al., 1994; Ulery et al., 1995; Certini, 2005; Verma and Jayakumar, 2012). Similar to pH, EC is also considered as ephemeral in nature as it has the tendency to step back to the pre-fire levels, over time (Ulery et al., 1993, 1995; Kim et al., 2003; Certini, 2005; Granged et al., 2011). Among the 18 sample stations, 7 stations displayed both increase in pH and EC, possibly due to the increase in fuel load, intense burn and the resulting addition of ash.

3.1.3. Soil organic matter (SOM)

The influence of forest fire on SOM is highly dependent on the intensity and types of fire, nature of fuels, soil moisture and many other factors so that generalised trends cannot be predicted (González-Pérez et al., 2004; Verma and Jayakumar, 2012). Low severity controlled burns result in a small change in the SOM, whereas a high severity fire

consume most of the organic matter (Johnson, 1992; Castro et al., 2011; Verma and Jayakumar, 2012). The SOM content in the study area (Fig. 4(c)) was measured using loss on ignition method and is reported as percentage (%). In the study area, 12 stations (67%) showed increase in SOM content after burn, whereas, 6 stations showed (33%) reduction in SOM. The increase may be due to the remains of burned organic matter from plants in the form of ash, while the reduction may be due to the removal of existing SOM by volatilisation. The highest variation observed is 24.44 followed by 24.43 and 19.8% and the lowest variation observed is 0.4%. Similar to pH and EC, the post-burn SOM increase is also ephemeral in nature, as it reduces with time due to the mobilization of ash (Hernández et al., 1997; Kim et al., 2003; Granged et al., 2011). In the pre-burn and post-burn environment, the highest SOM values were detected in samples collected close to the creek.

3.1.4. Carbonate content in soil

The measurement of carbonate (Carb) content expressed as % in the soil showed only minor variations before and after the burn (Fig. 4(d)). In the study area, 8 stations (44%) highlighted an increase and 10 stations (56%) highlighted decrease in carbonate content after the controlled burn. The highest variation observed between pre-burn and post-burn samples was 1.3% followed by 0.9% and the least variation observed was 0.11%.

The physicochemical properties of the surface soil is altered by the process of controlled burn such as organic matter combustion, heating and ash deposition (Certini, 2005; Verma and Jayakumar, 2012) and hence such changes are expected in the Maldon study area after the controlled burn. The data analysis clearly indicate that increase has observed in the soil pH, EC and OM in the post-burn environment (2 days after fire) compared to the pre-burn environment (2 days before burn) as noted by many authors (Hernandez et al., 2003; Certini, 2005; Quintana et al., 2007; Boerner et al., 2009; Verma and Jayakumar, 2012), but the carbonate content showed a reduction in the median value in the post-burn environment. The fire related pH and EC alterations (mainly increases) are mostly attributed to the combustion of forest fuels (plant materials including leaf litter), organic matter and the associated ash deposition (Ulery et al., 1993, 1995; Verma and Jayakumar, 2012; Campos et al., 2016).

3.2. Creek water pH and EC

When considering the median value of the creek water pH, there is no difference observed, however, individual testing stations showed increase of up to three units in pH value. Among the 11 water sampling stations, nine stations (82%) displayed an increase in pH.

When comparing the median EC value of the Creek water, the post-burn results displayed 38% increase, in such a way that all sampling stations displayed increased EC from 4 to 103 $\mu\text{S cm}^{-1}$. The increase in water pH and EC (Fig. 4(e) and (f)) is most probably attributed to ash particles during and after fire, which have high concentrations of cations, oxides, hydroxides and carbonates (Ulery et al., 1993, 1995; Goforth et al., 2005; Verma and Jayakumar, 2012). Similar outcomes were observed by Costa et al. (2014) with an increase in water pH and EC after fire, which were influenced by the transportation of ash and nutrients from the burned slope to the water resources. This immediate increase in water pH and EC is considered to be due to the mobility of ash through wind activity (in the absence of rainfall).

3.3. Physicochemical characteristics of ash

Ash is the solid material residue deposited on the soil surface from biomass burning, which consists of charcoal, charred organic material and residual mineral matter (Bodi et al., 2011; Pereira et al., 2014), and can deliver scientific information about fire influence on landscape. The ash presents as patches of white, grey and black colour and provides information about organic matter loss and fire severity (Blank and Zamudio, 1998; Keeley, 2009). Black ash contains a higher amount of charred organic materials and corresponds to a low to moderate fire severity, whereas, grey and white ash corresponds to high fire severity (Pereira et al., 2014). The major chemical constituents found in ash are Ca, K, Mg and P (Gabet and Bookter, 2011), and when blended with water the resulting slurry has a high pH value (Ulery et al., 1993). The pH, EC, organic matter (OM) and carbonate content of four ash samples collected just after the controlled burn are summarised in Table 2. The ash samples demonstrated high alkalinity with pH ranges from 9.1 to 11.4, and the EC ranges from 1173 to 28,500 $\mu\text{S cm}^{-1}$. The elevated pH and EC values of ash (compared with soils) are attributed to the formation of oxides, hydroxides and carbonates during the fire and the increase in amount of mineralised nutrients in ash (Ulery et al., 1995; Certini, 2005; Úbeda et al., 2009; Pereira et al., 2011; Verma and Jayakumar, 2012; Bodí et al., 2014). The OM ranged from 1.11% to 39.83% and the carbonate ranges from 10.37% to 37.77%.

The variations in ash properties are due to the amount of fuel burned, types of fuels, moisture content in the fuels, and fire severity in each sampling stations. The high pH value of ash 1 sample include a high carbonate content and grey colour demonstrated that this ash was produced at high temperature with high fire severity (Etiegni and Campbell, 1991; Ulery and Graham, 1993; Henig-Sever et al., 2001; Goforth et al., 2005; Pereira et al., 2008). The high OM content in ash 2 and its dark colour may be due to the incomplete combustion of vegetation (Goforth et al., 2005; Bodí et al., 2014). Similar to the case of soil, it is reported that ash pH, EC and OM also show ephemeral characteristics (Ulery et al., 1993; Campos et al., 2016).

3.4. Potentially toxic elements in pre-burn and post-burn soils

In the forest ecosystem, soil surface is considered the most affected area during forest fire (Mandal and Sengupta, 2006; Odigie and Flegel, 2014; Campos et al., 2015). The extend and severity of this burning affect varies with weather pattern, forest topography, vegetation types

and density, fire intensity, maximum temperature reached, soil moisture, amount of ash production, and post-fire climatic conditions (Certini, 2005; Maia et al., 2012; Verma and Jayakumar, 2012).

During any kind of forest fire, combustion of vegetation and soil organic matter, release the associated PTEs and convert them into a labile form, which increase the PTE mobility (Young and Jan, 1977; Certini, 2005; Biswas et al., 2007). During combustion, when the temperature reaches 180 °C, volatilization (slight distillation) of organic compounds begins, and this may continue up to 200 °C. This is followed by volatilization of nutrients, which starts at 200 °C and may continue up to 400 °C (Neary et al., 1999). In general, the influence of fire on organic matter comprises volatilization and charring, resulting in the partial or complete removal of forest floor litter (Simard et al., 2001), but organic matter recovery in the burned area is rapid through the natural and artificial reintroduction of vegetation (Certini, 2005). Fire can remobilize up to 85% of Hg and Pb as airborne components (dust and fly ash), whereas Cu and Co can be enriched in residue formed from the biomass burning (Narodoslawsky and Obernberger, 1996; Nzihou and Stanmore, 2013). This results in elevated concentrations in ash samples and rarity in post-fire soils (Costa et al., 2014; Campos et al., 2016). The elevated concentration of PTEs in ash make it as a primary source of post-fire PTEs, which can be effectively transported to distal areas (include downslope surface water resources) by rainfall runoff and wind activities (Yarmonenko, 2007; Bogacz et al., 2011; Campos et al., 2015, 2016).

When comparing the PTE concentrations in the pre-burn and post-burn soil environment, it has been shown that some of the PTEs have evidenced an increase in concentrations, while others decrease. Both can be considered as PTE mobility, especially if the difference in median values exceeds 10%. The descriptive statistics (minimum, maximum, range, median, percentiles and IQR) of pre-burn and post-burn PTE analysis data are depicted in Table 3 and summarised in Fig. 5. The median concentration of PTEs from highest to lowest in the pre-burn and post-burn samples were found to be in the same order (Mn > Zn > As > Cr > Cu > Pb > Ni > Co > Hg > Cd) and the post-burn concentrations of Zn, Mn, Cd, As, Ni, and Co were higher than their pre-burn concentrations, with values differing up to 7.8, 9.2, 10, 30.2, 3.8 and 3.9 times respectively. The concentrations of Hg, Pb and Cr were less in the post-burn samples, compared with pre-burn samples with values differing up to 2.2, 3.5 and 2 times respectively.

Zn demonstrated an increase in median concentration of 87% in the post-burn soil samples compared to the pre-burn samples. Twelve sampling station (66%) highlighted an increase in Zn concentrations, whereas other stations (44%) highlighted decrease. Zn in soil is more sensitive to soil pH changes than any other toxic element in the soil environment, and its mobility has also been found depend on soil pH (Chirenje et al., 2006).

When comparing the pre-burn and post-burn median Mn concentrations in the soil, the post burn soil showed 72% increase compared with pre-burn soils. Among the 18 sampling stations, 12 samples (66%) displayed increase in post-burn soil Mn concentration, which may be due to the presence of ash content in the soil as most of the Mn is reported to be stored in the plant leaves (Parra et al., 1996; Costa et al., 2014). The decrease in Mn concentration was observed in the sampling stations close to the creek, where leaf litter was comparatively lower compared to other soil samples. The highest Mn variation observed was 794 mg kg^{-1} at S3 and the least variation observed was 1 mg kg^{-1} at S16. The current increase in post-burn Mn concentration is supported by previous studies (Chambers and Attiwill, 1994; Parra et al., 1996; Costa et al., 2014).

Compared to other metals in this investigation, the concentration of Cd in the soil is very much lower. However, according to the median values, there was a 45% increase in Cd observed in the immediate post-burn environment, and it is noted that accumulation of Cd in the soil is related to sorption by SOM, clay mineral fixation and association with Mn oxides, Fe and Al oxides and hydroxides (Sipos et al., 2005; Kabata-Pendias, 2010).

Table 2
pH, EC, OM, carbonate content and colour of ash samples collected after the controlled burn.

Sample	pH	EC ($\mu\text{S cm}^{-1}$)	OM (%)	Carbonate (%)	Colour
Ash1	11.6	1173	1	38	Grey
Ash2	9.1	28,500	40	10	Light grey
Ash3	9.7	2600	19	19	Black
Ash4	9.6	18,900	18	17	black

Table 3Showing the minimum, maximum, range, median, percentiles and interquartile range (IQR) of pre-burn and post-burn potentially toxic element concentrations (mg kg^{-1}) in the soil.

	As-BF	As-AF	Cd-BF	Cd-AF	Co-BF	Co-AF	Cr-BF	Cr-AF	Cu-BF	Cu-AF
Minimum	19	12	0.03	0.01	4	3	23	15	14	6
Maximum	185	544	0.37	0.7	25	16	57	61	59	90
Range	166	533	0.34	0.69	21	13	34	46	45	84
Median	85	95	0.11	0.16	8	9	38	33	30	29
Percentiles										
10th	31	40	0.03	0.04	4	3	24	16	18	16
25th	63	63	0.07	0.09	6	7	33	29	20	21
50th	85	95	0.11	0.16	8	9	38	33	30	29
75th	141	126	0.19	0.24	11	13	46	41	44	47
90th	163	203	0.27	0.55	17	16	54	54	57	70
IQR	78	63	0.12	0.15	5	6	13	12	24	26
	Hg-BF	Hg-AF	Mn-BF	Mn-AF	Ni-BF	Ni-AF	Pb-BF	Pb-AF	Zn-BF	Zn-AF
Minimum	0.1	0.1	85	70	7	5	12	8	22	12
Maximum	9.4	9.9	560	7000	23	26	76	52	328	611
Range	9.3	9.9	475	6930	16	20	64	45	306	599
Median	2.2	1.6	191	329	13	14	30	25	94	176
Percentiles										
10th	0.4	0.1	89	112	8	6	18	17	33	32
25th	1.1	1.2	116	211	11	12	19	21	51	85
50th	2.2	1.7	191	329	13	14	30	25	94	176
75th	4.8	2.9	284	490	19	22	38	36	186	268
90th	7.8	4.7	470	1501	23	23	54	48	266	526
IQR	3.7	1.7	168	279	8	10	19	15	135	183

The median values demonstrated that in the immediate post-burn soil environment, As increased 11.5% compared to the pre-burn environment. Nine sampling stations (50%) displayed increases in As concentrations and 9 stations (50%) displayed decreases immediately after the burn. The increase in As concentrations in the post-burn environment may be associated with elevated As content in the ash by combustion of vegetation. Local vegetation may have absorbed As from the soil, where it was initially concentrated due to historical mining activities with gold bearing sulphides such as arsenopyrite (FeAsS), iron

pyrite (FeS_2), pyrrhotite (FeS), galena (PbS), sphalerite (ZnS) and chalcocite (CuFeS_2) (Sultan, 2006).

The Ni displayed a small increase (6%) in median concentration in the immediate post-burn environment. Similar to the case of Pb and Cd, Ni distribution and mobility may also depend on SOM, clay mineral and Fe oxides (Kabata-Pendias, 2010).

Regarding the Co concentration in the soil, the median showed only a slight increase (3.7%) in the burned soil as reported in previous studies (Costa et al., 2014; Campos et al., 2016).

When we compare the medians, Hg showed an overall reduction of 27% after the controlled burn with a minimum of 8% and maximum of 97% in the post-fire soils. Low concentrations of total Hg (THg) has been observed in ash samples and post-burn soil samples compared with pre-burn soil samples, and this is considered to be due to Hg volatilization during burning, as reported in previous studies (Biswas et al., 2007, 2008; Mergler et al., 2007; Burke et al., 2010; Melendez-Perez et al., 2014; Campos et al., 2015). The study of Biswas et al. (2007) supported this observation by noting 22–86% decrease in Hg concentration in the soil samples collected immediately after fire (IAF), and they added the observation that Hg mobility primarily depends on fire severity. However, additional studies are required in numerous soil types and numerous environmental circumstances to reconcile the differences between the laboratory and field studies.

In addition to Hg, other three elements have also shown decrease in median concentrations in the immediate post-burn environment: Pb showed 15%, Cr showed 12% and Cu showed only 2%, compared to the pre-burn environment.

The pre- and post-burn concentrations of PTEs in the soils of the 18 sampling stations demonstrated their mobility after the controlled burn. Among the 10 PTEs studied, Zn (87%), Mn (72%), Cd (45%), As (11.5%), Ni (6%) and Co (3.7%) demonstrated increase in their concentrations, whereas Hg (27%), Pb (15.4%), Cr (12%) and Cu (2%) demonstrated decrease in concentrations after the controlled burn. However, the mobility of Co, Ni and Cu are considered as small (as the mobility is found to be <10%). While Cu did not show significantly higher concentration in the post-burn soil, it showed high concentration (145 mg kg^{-1}) in the ash, which is consistent with other studies (Costa et al., 2014; Campos et al., 2016). Though soil pH strongly influences the adsorption, retention and mobility of the PTEs (Hernandez et al., 2003), such an association is not identified in the current post-

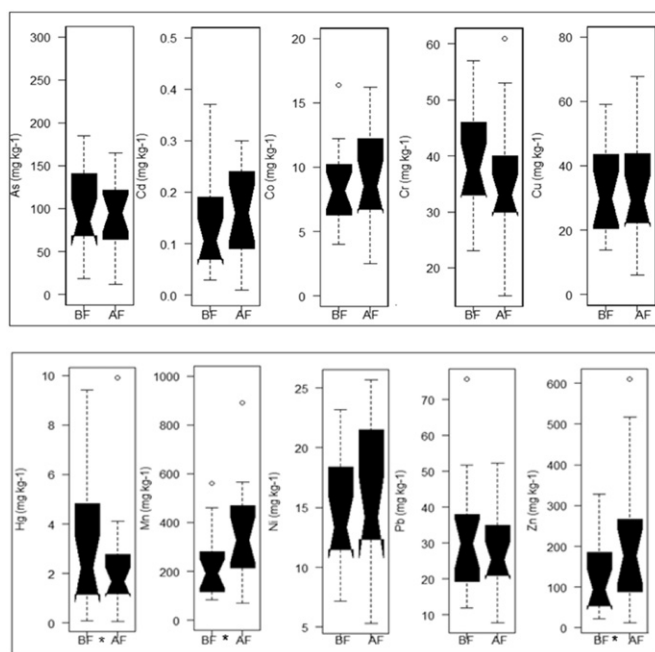


Fig. 5. Notched box plot showing the concentrations (mg kg^{-1}) of potentially toxic elements in the pre- and post-burn soil environment (Note: (i). 'o' denotes outliers, however in some plots outliers are away from figure as it exceeded the scale chosen, for example: As, Cd, Cu and Mn; (ii). "*" highlights the presence of statistically significant difference).

burn environment. This may be due to the immediate sampling which was done two days after the burn. Though the median levels of all PTEs demonstrated variations in the immediate post-burn environment, only difference in Zn, Mn and Hg levels are statistically significant ($p < 0.05$).

The quantity of PTE released through any kinds of forest fire primarily depends on the accrual and storage levels in the pre-fire environment, topography of the area, soil types and moisture content in the soil, types and amount of fuel, moisture content of fuel, weather pattern, temperature and duration of burning and maximum temperature reached (DeBano et al., 1998; Flannigan and Wotton, 2001; DeBano, 2000; Certini, 2005; Neary et al., 2005; Biswas et al., 2007). For example, in a laboratory study, soil released low amounts of Hg ($< 10\%$) when heated at 180°C for an hour, but four hours of heating at 320°C released $> 95\%$ of the THg from the soil (Biswas et al., 2007). Since fire intensity and duration of heating is less in a controlled burns compared to wild fires, it is not severe enough to remobilize most of the PTEs sequestered in forest vegetation and soil organic matter specifically from the lower and middle layers of the forest floor (Nriagu, 1996; Shcherbov, 2012; Sen and Peucker-Ehrenbrink, 2012).

3.5. Potentially toxic elements in ash

The heterogeneous residue left at the soil surface after the forest fire known as 'ash', gives a general impression of the forest fire. It is a key component to addressing PTEs mobility on the landscapes, as most of the forest fire ash contains elevated concentration of PTEs (Plumlee et al., 2007; Pereira and Ubeda, 2010; Odigie and Flegal, 2011, 2014). It represents the enduring accumulation and storage of mineral matter in soil organic horizon and of the vegetation in the pre-fire environment, include PTEs and other contaminants (Someswar, 1996; Johansen et al., 2003; Goforth et al., 2005; Biswas et al., 2007; Campos et al., 2012; Wade et al., 2013; Campos et al., 2015, 2016).

The descriptive statistics of PTE concentration in ash is depicted in Table 4. The ash left after the controlled burn revealed perceptible differences in physicochemical properties and the PTE concentrations compared to post-fire soil. Based on the PTE analysis data it was found that Mn (from 330 to 2790 mg kg^{-1}) achieved the highest concentration and Zn (from 221 to 555 mg kg^{-1}) achieved the second highest concentrations in ash, whereas, Cd (0.02 to 0.22 mg kg^{-1}) and Hg (0.02 to 0.41 mg kg^{-1}) represent the lowest concentrations. The highest Mn concentration in ash is supported by other studies (Costa et al., 2014; Campos et al., 2016). There are appreciable quantities of Cu (56.1 to 207 mg kg^{-1}) and As (20.08 to 260 mg kg^{-1}) also found in ash. It is noteworthy that the As concentration in the ash is elevated so that this presents a vector for As redistribution in the atmosphere, soil and downstream water resources. The median concentration of Mn, Zn, Cu and Ni in ash is found to be higher than their concentration in the soil, whereas, the concentration of As, Cd, Co, Cr, Hg and Pb are found to be higher in soil than in ash. The varying concentrations of PTEs in ash depends upon many natural factors such as meteorological conditions, pre-fire metal concentrations (in the soil, soil organic matter, and in vegetation), age and vegetation density in the forest ecosystems, vegetation parts burned (like bark, leaves and litter), duration of the burning, fire intensity, maximum temperature reached, soil types, and moisture content in the soil (Someswar, 1996; Pereira et al., 2009; Pereira and Ubeda, 2010; Machado et al., 2015).

Table 4
Concentrations of potentially toxic elements (mg kg^{-1}) in ash.

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Median	23	0.1	9	9	145	0.04	1270	28	5	475
Range	239	0.2	7	4	151	0.4	2460	28	13	334
IQR	180	0.2	5	3	114	0.3	1990	25	10	277

NB: IQR - interquartile range.

Previous studies revealed the presence of PTEs (Mn, Zn, Cu, Pb, Hg, Cd and As) in ash samples found in forests across the globe (Ferreira et al., 2005; Plumlee et al., 2007; Pereira and Ubeda, 2010; Bogacz et al., 2011; Odigie and Flegal, 2011, 2014; Campos et al., 2016). To illustrate this, Plumlee et al. (2007) reported significantly elevated concentration of PTEs (As up to 140 mg kg^{-1} , Pb up to 344 mg kg^{-1} , Cu 1370 mg kg^{-1} and Zn up to 2800 mg kg^{-1}) in ash samples after the southern California forest fire in USA that persisted for a year following the fire. Similarly, distribution of Co (3 – 11 mg kg^{-1}), Cu (15 – 69 mg kg^{-1}), Ni (6 – 15 mg kg^{-1}), Pb (7 – 42 mg kg^{-1}) and Zn (65 – 500 mg kg^{-1}) were observed in ash after the Williams fire in Los Angeles (2012), USA (Odigie and Flegal, 2014) and Kristensen et al. (2014) reported mobilization of natural and industrial Pb in ash samples after three large uncontrolled intense wildfire events (February 2011) in Australia. Many of the metal mobilization studies highlighted Mn as being present in the highest concentration (Parra et al., 1996; Costa et al., 2014; Campos et al., 2016). For example, highest levels of Mn (121 – 448 mg kg^{-1}) in ash were reported by Costa et al. (2014) after the Marao Mountain forest fire and Campos et al. (2016) reported 57 – 598 mg kg^{-1} of Mn in ash after the Ermida fire, both in Portugal. The increase in concentration of Mn in ash is linked to combustion of plant leaves as it is a component of the photosynthesis (the water splitting complex) (Kabata-Pendias, 2010; Farzadfar et al., 2017; Shao et al., 2017). Studies emphasised that PTEs formed in ash during fire may be remobilised through post-fire rainfall runoff and wind activities (Smith et al., 2011; Stein et al., 2012; Costa et al., 2014; Campos et al., 2016; Abraham et al., 2017a, 2017b). Thus, forest fires include controlled burns, can be considered as a vector for environmental alterations that may influence human and ecosystems health.

3.6. Relationship of potentially toxic elements in soil and ash with physico-chemical characteristics

The relationship between PTE concentrations in pre-burn and post-burn soil (Table 5) and ash (Table 6) with physicochemical characters such as pH, EC, SOM and carbonate contents were assessed with Spearman rank correlation method using R (3.4.1). The results do not identify any statistically significant very strong ($r = 0.80$ – 1.0) and strong ($r = 0.60$ – 0.79) correlations between physicochemical properties of soil and PTEs in the pre- and post-burn environments, except pH with Ni and Co, however PTEs themselves shown very strong and strong correlations.

When we consider pH, it showed a strong correlation with Ni ($r = 0.62$) and Co ($r = 0.61$), and a moderate ($r = 0.40$ – 0.59) correlation with Cr ($r = 0.54$) and Zn ($r = 0.46$) in the pre- and post-burn soils. Similar relation between soil pH with Ni and Co were also reported by Wilde et al. (2004). The soil EC does not show any significant correlation with any of the PTEs in both pre- and post-burn environments, but SOM displayed moderate correlations with Cd ($r = 0.53$), Cu ($r = 0.51$), Ni ($r = 0.50$), Zn ($r = 0.49$) and Cr ($r = 0.44$) in the pre- and post-burn environments. Similar to SOM, carbonate also exhibit moderate correlation with number of PTEs, including Cr ($r = 0.57$), Ni ($r = 0.50$), Cu ($r = 0.48$), Pb ($r = 0.48$), Co ($r = 0.46$), Mn ($r = 0.45$), Cd ($r = 0.43$) and Zn ($r = 0.40$) in both pre- and post-burn soil environments.

The correlations between PTEs (themselves) in the pre- and post-burn soil environments are almost similar in value (Table 5), and the strong and very strong correlations highlight their common origin. The very strong correlation of As with Mn ($r = 0.80$) shows that Mn is a significant element in the soil, which controlling the mobility of arsenate (an abundant form of As), which is also reported by Sultan (2007). The strong correlation of As with Pb ($r = 0.77$) and Zn ($r = 0.76$) revealed their common origin in the Ordovician sedimentary rock during gold mineralization in association with galena (PbS) and sphalerite (ZnS). As also shown strong correlation with Cd ($r = 0.75$), Co ($r = 0.65$), Hg ($r = 0.63$) and Cu ($r = 0.60$) revealed the legacy mining activity. Mn demonstrated strong correlation with Cd ($r = 0.73$), Co (0.73),

Table 5

Spearman rank correlation coefficient between the physicochemical properties of soil and PTEs in the pre-burn (above diagonal elements) and the post-burn (below the diagonal elements) environment.

	pH	EC	SOM	Carb	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
pH		−0.48	0.43	0.04	0.32	0.37	0.61	0.54	0.38	0.02	0.35	0.62	−0.04	0.46
EC	−0.48		0.28	0.37	−0.23	−0.10	−0.03	−0.02	0.14	−0.08	0.04	−0.08	−0.03	−0.21
SOM	0.43	0.28		0.37	0.10	0.53	0.38	0.44	0.51	−0.03	0.36	0.50	0.28	0.49
Carb	0.04	0.38	0.37		0.32	0.43	0.46	0.57	0.48	0.13	0.45	0.50	0.48	0.40
As	0.32	−0.23	0.10	0.32		0.75	0.65	0.48	0.60	0.63	0.80	0.53	0.77	0.76
Cd	0.37	−0.10	0.53	0.43	0.74		0.70	0.66	0.72	0.46	0.73	0.75	0.75	0.98
Co	0.61	−0.03	0.38	0.46	0.65	0.70		0.86	0.76	0.25	0.73	0.94	0.30	0.76
Cr	0.54	−0.02	0.44	0.57	0.48	0.66	0.86		0.77	0.04	0.47	0.95	0.32	0.72
Cu	0.38	0.14	0.51	0.48	0.60	0.72	0.76	0.77		0.37	0.58	0.79	0.46	0.74
Hg	−0.02	−0.08	−0.03	0.13	0.63	0.46	0.25	0.04	0.37		0.49	0.12	0.51	0.43
Mn	0.35	0.04	0.36	0.45	0.80	0.73	0.73	0.47	0.57	0.49		0.61	0.62	0.71
Ni	0.62	−0.08	0.50	0.50	0.53	0.75	0.94	0.95	0.79	0.12	0.61		0.32	0.82
Pb	−0.04	−0.03	0.28	0.48	0.77	0.75	0.30	0.32	0.46	0.51	0.62	0.32		0.67
Zn	0.46	−0.21	0.49	0.40	0.76	0.98	0.76	0.72	0.74	0.43	0.71	0.81	0.67	

Note: Very strong ($r = 0.80$ – 1.0) and strong ($r = 0.6$ – 0.79) correlations are in bold.

Zn (0.71), Pb (0.62) and Ni (0.61) considered to be due to the specific absorption capacity of Mn oxides to these elements (Cd, Co, Zn, Pb and Ni).

The physicochemical properties of ash and PTEs in the ash display a number of very strong and strong correlations, and all these significant correlations are highlighted in Table 6 for easy reference. In the ash samples, pH displayed strong positive correlation with Co ($r = 0.80$) and strong negative correlation with Cu ($r = -0.80$) and Zn ($r = -0.80$), however, EC shown strong positive correlation with Cu ($r = 0.80$) and Zn ($r = 0.80$) and strong negative correlation with Co ($r = -0.80$). SOM has very strong correlation with Zn ($r = 1.0$) and strong negative correlation with Cr ($r = -0.74$). Carbonate also follow similar kind of very strong positive correlation with Co ($r = 0.80$) and very strong negative correlation with Cu ($r = -0.80$) and Zn ($r = -0.80$).

Previous studies noted that physicochemical characteristics such as pH, EC and OM of soil perform a significant part in the retention and mobilization of PTEs in the soil environment (Chlopecka et al., 1996; Mehes-Smith et al., 2013). In this study, however, no significant very strong correlation was observed between physicochemical parameters of soil and PTEs in the soil (except few strong and a number of moderate and weak relationships), similar to the studies of Wang et al. (2010).

4. Conclusion

Detailed analysis of PTE dynamics relevant to the effects of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn on the environment, is crucial for ecosystem management and sustainability. The overall increase in concentrations of PTEs such as Zn, Mn, Cd, As, Ni and Co, together with changes in physicochemical characteristics of soil including pH, EC and SOM in the

post-burn soil environment, highlight that a controlled burn acts as a mobility vector and a source of PTE contamination. In addition, ash formation during fire, and its propensity for mobility influences the PTE concentration in the adjacent soil, water and air environments. Results of this study showed that ash was consistently enriched in PTEs compared to the underlying and adjacent surface soil, signifying that the accumulation of ash on soil and water surfaces can contribute to an increase in PTE concentration in the post-burn environment. The increase in soil pH, EC, SOM and the increase in water pH and EC is also attributed to the presence of ash, which has elevated quantities of oxides, hydroxides, carbonates and many other minerals and nutrients.

The observed decrease in levels of Hg and Pb in the post-burn soil environment, suggests that volatilization of these elements have taken place during fire. This PTE mobility has substantial implications in the environment due to its influence on all aspects of biota from soil microbes to terrestrial and aquatic vertebrates, including humans and ecosystem resilience in general. For example, Hg is of particular concern in the post-burn environment, specifically in wetlands, because the physicochemical and biological conditions are favourable for the formation of methyl Hg (MeHg), which has severe neurological implications for organisms, and may also reach the human consumer. As a consequence, controlled burning, and the resulting PTE mobility, highlights significant concern given the impacts of these toxic elements to human and ecosystem health. This is particularly relevant given that controlled burning is increasingly being used over large areal extents in fire-prone areas, and is also often used in proximity to human settlements as a standard fire risk reduction strategy. Such changes in use and extent of controlled burns will release and remobilize greater volumes of PTEs into the environment, which is of some concern. Therefore, information regarding

Table 6

Spearman rank correlation coefficient between the physicochemical properties of ash and the PTEs in ash.

	pH	EC	OM	Carb	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
pH	1													
EC	−1.0	1												
SOM	−0.80	0.80	1											
Carb	1.0	−1.0	−0.80	1										
As	0.40	−0.40	−0.20	−0.40	1									
Cd	0.20	−0.20	−0.20	−0.40	0.20	0.80	1							
Co	0.80	−0.80	−0.40	0.80	0.00	−0.40	1							
Cr	0.21	−0.21	−0.74	0.21	0.11	0.63	−0.32	1						
Cu	−0.80	0.80	0.40	−0.80	−0.80	−0.40	−0.60	0.11	1					
Hg	0.40	−0.40	−0.20	0.40	1.0	0.80	0.00	0.11	−0.80	1				
Mn	−0.20	0.20	0.40	−0.20	−0.80	−1.0	0.40	−0.63	0.40	−0.80	1			
Ni	−0.20	0.20	0.40	−0.20	−0.80	−1.0	0.40	−0.63	0.40	−0.80	1.0	1		
Pb	0.40	−0.40	−0.20	0.40	1.00	0.80	0.000	0.11	−0.80	1.00	−0.80	−0.80	1	
Zn	−0.80	0.80	1.00	−0.80	−0.20	−0.40	−0.40	−0.74	0.40	−0.20	0.40	0.40	−0.20	1

Note: Very strong ($r = 0.8$ – 1.0) and strong ($r = 0.60$ – 0.79) correlations are in bold.

PTEs mobility associated with controlled burning is a significant contribution to managing environmental and ecosystem health and sustainability.

It has been shown that PTE concentrations in post-burn environments are directly linked to their original concentration in the pre-burn environment. This means that if the pre-burn soil has elevated amounts of PTEs, such as found in legacy mine sites or any kinds of mining or industry-affected landscapes, the mobilization of the PTEs will also be elevated during, or after, the controlled burn. As a consequence, the possible local effects of the resulting PTE mobility, with its related health impacts on human and ecosystems, must be carefully examined and due vigilance must be applied before any controlled burns are to be used to provide an effective forest management tool in mining-affected landscapes.

Conflict of interest

The authors declared that they have no conflict of interest.

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